Title: "Investigations on Electrical and Electrochemical Properties of Hot Pressed Solid State Ionic Electroactive Polymeric Membranes"

1. Introduction: Solid State Ionic Materials

Solid State Ionics, one of the frontline areas in the Materials Science research, mainly deals with the solid systems which exhibit fast ion transport within the bulk. It is truly an interdisciplinary area of research to investigate the physical, chemical, engineering as well as technological aspects of such materials. Solid State Ionics materials, popularly know as **Superionic Solids** or **Fast Ion Conductors** or **Solid Electrolytes,** exhibit room temperature conductivity (σ_{rt}) quite close in the range that of liquid /aqueous electrolytes. Hence, they are looked upon as potential/promising candidates to replace liquid/aqueous electrolytes in the fabrication of All-Solid-State electrochemical devices viz. batteries, fuel cells, super-capacitors, sensors, electro-chromic displays etc. [1-9]. Historically, fast ion conduction in solids was reported for the first time in 1839 by Faraday [10] in Ag_2S when it was hot. Much later, Tubant & Lorenz in 1914 [11] reported exceptionally high Ag^+-ion conduction (σ ~ 1S/cm) in AgI when heated beyond 147^0C. In fact, at 147^oC AgI undergoes a well known characteristic structural phase transition from a low conducting β- / γ - phase to superionic α-phase which is accompanied with 3-4 orders of magnitude vertical jump in conductivity. Number of attempts were made afterwards to bring down α-phase conduction of AgI to room temperature as well as to explore for other materials exhibiting superionic conduction at lower temperatures. Subsequently, the real breakthrough occurred in the year 1967 after the discovery of two groups of solids: MAg_4I_5 (M = Rb, K, NH_4) [12,13] and Na-β-Alumina [14] which were reported to exhibit exceptionally high Ag^+- and Na^+- ion conduction (~10^{-1}-10^{-2} S/cm) at room/slightly elevated temperatures respectively. This remarkable discovery brought a big boost in the activity in this branch of materials science research world-wide. As a result, in the last nearly five decades, a wide variety of superionic solids involving different kinds of mobile ion species viz. H^+, Ag^+, Cu^+, Li^+, Na^+, K^+, F^-, O^{-2} etc. has been investigated and their potential applicabilities in variety of solid state electrochemical devices have been comprehensively tested [1-9]. Based on physical characteristics, their microstructure and synthesis route, these materials have been grouped into following broad categories:

- Framework crystalline/polycrystalline electrolyte phase
- Glassy/amorphous electrolyte phase
- Composite electrolyte phase
- Polymer electrolyte phase

In the present thesis, the field of Solid State Ionics has been reviewed extensively along with giving description on the designing different electrolyte phases. Since, this Ph.D. work has been mainly focused on the polymer electrolyte materials, hence, a detail discussion has been made on this class of electrolyte phase separately. A brief mention on above category of solid electrolyte phases has been made below.

(i) Framework Crystalline/ Polycrystalline Solid Electrolytes: Framework crystalline / polycrystalline solid electrolytes are microscopically ordered phase in which ions move more or less in the rigid crystalline framework. However, they usually possess two sub-lattices: a rigid cage like skeleton sub-lattice and a molten sub-lattice enclosed within, which facilitate liquid like transport of ions. These solid electrolytes are synthesized, in general, by solid solution reactions of two or more ionic salts. This solid electrolyte phase has been further divided into two subgroups viz, **Soft-framework materials** and **Hard-framework materials.**

(ii) Glassy/ Amorphous Solid Electrolytes: The glassy/ amorphous electrolytes are microscopically disordered phase and generally synthesized by rapid quenching/ cooling the homogeneous molten mixture of three basic constituent materials: a Host Salt viz. AgI, CuI, LiI etc. a Glass Modifier [GM] viz. Ag_2O, Cu_2O, LiO_2 etc. and a Glass Farmer [GF] such as B_2O_3, MoO_3, V_2O_5, P_2O_5, ZrO_2 etc. which are taken in appropriate mol. wt. (%). The quick/ sudden cooling of melt results into short range order and microscopically disorder glass/amorphous structure. Kunze in 1973[15] for the first time discovered fast Ag^+ -ion conduction ($\sigma_{rt} \sim 10^{-2}$ S/cm) in (AgI : Ag_2SeO_4) after melt-quenching.. Since then, a large number of glass electrolytes involving different mobile ion species viz. Ag^+, Cu^+ , Li^+, Na^+, F^- etc has been discovered. This phase has several materials advantages over other solid electrolyte phases.

(iii) Composite Solid Electrolytes: Composite solid electrolytes, also referred to as '**dispersed solid electrolytes**', are multi-phase (mostly two phase) solid systems. These solid electrolytes attracted great deal of technological attentions after C.C. Liang [16] reported ~ 50 times enhancement in Li^+- ion conduction at room temperature in LiI dispersed with submicron Al_2O_3 particles. This was a 2-phase inorganic composite

electrolyte in which LiI acted as I^{st}-phase host and Al_2O_3 as a II^{nd}-phase dispersoid. In 2-phase composite electrolyte systems, usually I^{st}-phase host is a moderate ion conducting salt viz. alkali / silver / copper halide and II^{nd}-phase dispersoid is an inert/insulating materials such as Al_2O_3, SiO_2, TiO_2, ZrO_2 etc. As a consequence of dispersal of submicron (μm / nm) size particles of II^{nd}-phase (in small fraction) into I^{st}-phase host salt, a substantial improvement in σ_{rt} (~ 1- 3 order of magnitude) as well as other physical properties of the host is normally achieved. These inorganic composite electrolytes are macroscopically disordered in structure and both the phases coexist together separately without any structural / chemical modifications. Large number of 2-phase inorganic composite electrolytes involving different mobile ions viz. Ag^+, Cu^+, Li^+, Na^+ etc. have been reported in the last ~ 4 decades and their applications in all-solid-state electrochemical devices have been investigated.

(iv) Polymer Electrolytes: Polymer Electrolytes in thin/flexible film form are novel and exotic materials with tremendous technological promises. They are ion conducting electroactive polymeric membranes exhibiting moderately high ionic conductivity ($\sigma_{rt} \leq 10^{-4}$ Scm^{-1}) at room temperature and possess several advantageous materials merits over the other solid electrolyte phases. They exhibit liquid like ionic conductivity as well as solid like mechanical integrity and are looked upon as appropriate alternate choice as solid electrolyte for the development of All-Solid-State thin film electrochemical devices viz. batteries in any desired shapes/sizes including mini/micro/ printable batteries. As already stated, since my Ph. D. work is mainly aimed at investigations on this class of materials; hence, a detailed discussion on this electrolyte phase has been made below.

2. Polymer Electrolytes

Amongst the various solid electrolyte phases mentioned above, polymer electrolyte phase possesses several advantageous material properties over others. They possess thin/ flexible/ laminar structure with high mechanical/ chemical/ thermal stability. Hence, as mentioned, they can be used to develop all-solid-state flexible/ compact/ light weight/ leak proof electrochemical power sources viz. mini/ micro thin film primary/ secondary batteries, fuel cells, supercapacitors etc. in any desired shapes/ sizes. The first polymer electrolyte i.e. 'PEO (polyethylene oxide) complexed with alkali metal salt' was discovered in 1973 by Fenton et al [17]. However, the technological relevance of this electrolyte phase was recognized only after the practical demonstration of all-solid-state battery based on 'polymer PEO complexed with Li^+- ion salt' in 1979 by Armand et al [18]. Since then, a

wide variety of polymer electrolyte materials involving different kinds of mobile ion species viz. H^+, Li^+, Na^+, K^+, Ag^+, Mg^{2+} etc. has been reported in the last nearly four decades [19,20]. The Polymer electrolyte systems can be classified into following five broad categories:

● **Conventional polymer-salt complexes or Solid Polymer Electrolytes (SPEs)**

They are dry polymer electrolyte membranes in which ionic salts having large size anions are intentionally chosen for complexing/ dissolving into a high molecular weight polar polymeric host. SPE membranes are usually cast using the traditional solution-cast method. However, very recently hot-press technique, a completely dry/ solution free procedure, is employed widely for casting these films.

● **Plasticized Polymer Electrolytes (PPEs):** They are prepared by adding small amount of low molecular weight solvents such as Ethylene Carbonate (EC), Propylene Carbonate (PC), Dimethylfarmamide (DMF) etc. into solid polymer electrolytes (SPEs). This is also referred to as 'solvent-swollen polymer electrolyte'. A significant enhancement in the room temperature conductivity could be achieved but at the cost of compromising the mechanical integrity of the membrane as well as increased corrosive reactivity of the electrolyte towards the electrodes during device application.

● **Gel Polymer Electrolytes (GPEs):** Polymer gel electrolytes are usually formed by adding large amount of solvent dissolving the salt in the polymer matrix and left for gellification. They also exhibit high room temperature conductivity, but encounter the same drawbacks as mentioned above for the plasticized polymer electrolytes.

● **Rubbery Polymer Electrolytes (RPEs):** Contrary to solid polymer electrolyte which contains small amount of salt with large amount of polymeric host, rubbery electrolytes are prepared by mixing large amount of salt with a small amount of polymer. These electrolytes are referred to as "polymer-in-salt" systems, in contrast to "salt-in-polymer" SPE systems. They also exhibit high ambient conductivity; rubbery state is maintained due to low glass transition temperature (T_g) of polymer host. However, the complexing salt in rubbery electrolytes invariably tends to get crystallized with time which seriously hampers their use in practical devices.

● **Composite Polymer Electrolytes (CPEs):** Composite polymer electrolytes, akin to two-phase inorganic composite electrolytes, can be regarded as two-phase organic composite electrolytes in which SPE acts as I^{st} -phase host matrix and submicron (μm/nm) size particles of inert/ insulating inorganic filler material such as Al_2O_3, SiO_2, TiO_2, $BaTiO_4$, MgO etc. as II^{nd} -phase dispersoid. As a consequence of dispersal of fractional amount of

filler material into Ist-phase SPE, the room temperature conductivity of SPE host gets substantially increased along with the improvements in other physical properties of polymeric electrolyte membrane such as mechanical integrity, electrode–electrolyte compatibility/ reactivity etc. The particle size of the filler material and the chemical nature i.e. Levis acid-base reaction between polymer chain and dissociated salt play important role in controlling these improvements. It has usually been noticed that smaller is the particle, larger is the improvement in the physical properties of SPE. SPEs dispersed with the submicron filler particles are referred, in general, to as Composite Polymer Electrolytes (CPEs), and when nano particles are dispersed they are called Nano Composite Polymer Electrolytes (NCPEs). The additive filler material can be classified as active or passive. The active fillers are those which contribute mobile ions for conduction.

3. Summary of Total Work-done in Present Ph. D. Programme

As already pointed out earlier, the present Ph.D. work has been mainly aimed at investigation on polymeric electrolyte systems i.e. synthesis of SPE/NCPE films and characterization of the materials/ ion transport properties as well as study of All-Solid-State battery performance.

The total work done in the present Ph.D. programme has been summarized below in the following sub- sections along with the broad objectives.

3.1 Broad Objectives

- **Synthesis of non-lithium chemical based dry polymer electrolytes(SPEs/ NCPEs)**

Solid Polymer electrolyte (SPE) films : (PEO: $AgCF_3SO_3$)

: (PEO: $AgClO_4$)

Nano Composite Polymer Electrolyte (NCPE) films: (PEO: $AgCF_3SO_3$) + x Al_2O_3

: (PEO: $AgClO_4$,) + x TiO_2

These films have been synthesised primarily using hot-press technique. However, for the sake of comparing quality and σ_{rt}- value of hot-press cast films, some of the optimum conducting SPE/NCPE films have also been prepared by traditional solution cast method. A high mol. wt. polar polymer: poly (ethylene oxide) PEO has been used as host in common, non-lithium salts viz. $AgCF_3SO_3$ and $AgClO_4$ as complexing salts and nano particles of filler materials: Al_2O_3 and TiO_2 as dispersoid.

➢ **Identification of optimum conducting SPE/NCPE films**

SPE films exhibiting optimum σ_{rt} have been identified from salt- concentration dependent conductivity studies. Using these SPE film compositions as I^{st}- phase host and nano-filler particles as II^{nd} – phase dispersoid, NCPE films have been hot-press cast and Optimum Conducting Composition (OCC) NCPE films have been identified form filler-particle-concentration dependent conductivity studies.

➢ **Characterization of materials/ion transport properties in SPE (I^{st}-phase)/NCPE OCC films**

- Materials and structural characterizations in SPE hosts and NCPE OCC films have been done employing XRD/SEM/FTIR techniques and thermal analysis by DSC.

- The characterization of ion transport properties in the newly synthesised Ag^{+}- ion conducting SPE hosts and NCPE OCC films has been carried out in terms of basic ionic parameters viz. ionic conductivity (σ): measured by ac method at a fixed frequency, total ionic transference number (t_{ion}) : by dc polarization TIC technique, cation transference number (t_{+}): by combined ac/dc method.

- The temperature dependent conductivity measurements have also done in order to understand ion transport behaviour. The activation energy (E_a) involved in the thermally activated process has been computed by linear least square fitting of the slope of 'log σ -1/T' Arrhenius plot.

➢ **Characterization of Electrochemical behaviour in SPE(I^{st}-phase)/NCPE OCC films**

Finally, using SPE hosts and NCPE OCC films as electrolyte, All-Solid-State batteries have been fabricated by sandwiching the film in between appropriate anode/cathode couple and the electrochemical cell performance has been studied under varying load conditions.

➢ **Study of nano-ionic effect in SPE film: An additional work**

Besides above studies, in order to investigate nano-ionic effect, which may lead to further enhancement in σ_{rt}, an additional work has been carried out on Cu^{+} -ion conducting dry solid polymer electrolyte films, based on PEO as polymeric host and $C_2H_3CuO_2$ as complexing salt. These films have been prepared by hot-press method and

the optimum conducting SPE film has been identified, as before The nano-ionic (I) effect in this optimum conducting SPE film has been introduced through high energy ball-milling of powder mixture of this film composition, prior to hot-press casting the film. Rest of the characterization studies have been similar to those mentioned above for SPE/NCPE film. As a consequence of high energy ball milling, a substantial enhancement in σ_{rt} has been achieved.

3.2 Methodology adopted in the present Ph.D. programme: The total work carried out in the present Ph.D. programme is discussed below in brief.

As mentioned in the broad objective, following two dry polymer electrolyte (SPE/NCPE) films have been hot-press synthesised:

SPE Films	NCPE Films
• PEO: $AgSF_3SO_3$	• (PEO: $AgClO_4$) + TiO_2
• PEO: $AgClO_4$	• (PEO: $AgSF_3SO_3$) +Al_2O_3

High molecular weight polar polymer poly(ethyleneoxide) PEO has been used as host matrix in common and Ag^+ ion conducting salts: $AgSF_3SO_3$ and $AgClO_4$ as complexing salts. Optimum room temperature conducting SPE films (to be used as I^{st} –phase host) have been identified by salt-concentration dependent conductivity measurements. NCPE films have been prepared after dispersing nano-particles of Al_2O_3 and TiO_2 as II^{nd} – phase dispersoid into I^{st}-phase SPE hosts and NCPE OCC films have been identified by filler particle concentration dependent conductivity measurements. In order to compare the quality and σ-value of hot-press cast films, the optimized SPE/NCPE films have also been prepared by the traditional solution cast procedure. Film casting procedures viz solution cast and hot-press methods, are discussed below along with their merits and demerits.

(a) Solution cast method: In this procedure, dry powders of polymer and complexing salt (in appropriate mol wt. % / wt. %) are dissolved separately in a common solvent (viz. methanols, double distilled water, acetonitrile etc.). The two solutions are then mixed together and stirred magnetically at room or at a slightly elevated temperature for sufficient time (few hours to few days) ensuring that the salt complexation in the polymer host has been completed. For casting Composite Polymer Electrolyte (CPE)/ Nano composite Polymer Electrolyte (NCPE) films, micro/nano sized filler particles are

added to (polymer + salt) solution mixture during stirring. The obtained viscous solution is then poured into the petri-dishes for casting SPE/CPE / NCPE films through slow evaporation of the solvent. Film of uniform thickness ~ 100-200 μm are usually obtained by this method.

(b) Hot-press method: Hot-press technique for casting dry polymer electrolyte films has recently gained wide acceptability. For hot-press casting SPE film, dry powders of polymeric host and salt in appropriate wt. / mol. wt. (%) ratios are mixed physically for about ~30-60 min. The homogeneously mixed powder is then heated close to the melting point of polymeric host, with mixing continued for ~ 30-40 min. This gives rise to a soft slurry/ lump of polymer complexed with salt which is then pressed (~ 1-2 ton / cm^2) between two cold SS blocks resulting into a uniform thin SPE membrane of thickness ~ 100-150 μm. For hot-press casting of NCPE film, II^{nd}-phase dispersoid filler materials in appropriate (wt. % / mol. wt. %) proportion is added to optimum conductivity SPE film composition, which acts as I^{st}-phase host, followed by heating around the melting / softening point of polymer and then pressed to form film, as before. The total time required for hot-press casting of SPE/NCPE films is approximately 1-2 hours. It is completely dry/solution-free and much quicker procedure with least consumption of chemicals, hence, preferred over the traditional method for casting dry polymer electrolyte films.

Dry Polymer electrolyte (SPE/NCPE) films reported so far usually show $\sigma_{rt} \leq 10^{-4}$ S/cm & $t_+ < 0.5$ However, for practical device applications σ_{rt} & t_+ values should be $>10^{-4}$S/cm & > 0.5 respectively. In order to achieve these values in dry polymer electrolytes a possible way suggested in the literature would be to introduce nano-ionic (I) effect in these system [21-23]. This can be done through high energy ball-milling of dry powder mixtures of polymer host + complexing salt (+ filler particles) prior to casting the films. Hence, in the present Ph.D. program, in order to study this effect, an additional dry polymer electrolyte system has been hot-press cast after introducing nano-ionic (I) effect. This is an additional study reported in this thesis and discussed below in brief.

Nano-ionic effect in dry polymer electrolyte through high energy ball milling: Firstly, SPE films: (PEO: $C_2H_3CuO_2$) in varying salt concentration have been hot-press cast. The film exhibiting optimum conductivity at room temperature has been identified, as before. The powder mixture of this film composition has been subjected to high

energy ball milling for different durations viz. 0, 2,4,6,8,10,12,14. hrs. Here, 0-hr-milling referred to an unmilled sample which is a simple physical mixture in agate mortar/pestle for 30-60 min. The milling was performed in a dry atmosphere using a twin planetory – ball mill machine operating at 400 rpm. A tungsten carbide bowl (250ml) and 2-4 tungsten carbide balls of ~ 10nm diameter have been used for milling the powder mixture. The ball milled sample powder was subjected to hot-press casting of SPE film as before and then for different characterization studies.

3.3 Materials characterization studies: In order to confirm the complexation of salt in polymer host as well as dispersal of filler particles in the SPE host, characterizations of structural/ morphological/ vibrational/ thermal properties of the polymer electrolyte film materials have been done with the help of XRD/SEM/FTIR/DSC techniques. Since degree of amorphous phase in the polymeric host controls the order of conductivity enhancement in these systems, the information regarding degree of amorphousity can be evaluated with the help of XRD/ DSC analysis.

3.4 Characterization of ion transport properties: Ion transport property of the newly synthesized SPE/NCPE films have been characterized in terms of some basic ion transport parameters viz. ionic conductivity (σ), total ionic transference number (t_{ion}) and cationic transference number (t_+) etc. The temperature dependent conductivity measurements have also been done and the activation energy (E_a) has been computed form 'logσ- 1/T' Arrhenius plot. These studies provide information regarding the mechanism of ion transport within the bulk of polymeric electrolyte systems. Different experimental techniques, employed to evaluate these ionic parameters, are discussed below in brief.

- **Conductivity measurement:** This is done usually by ac Impedence spectroscopy (IS) in which the real and imaginary impedances are measured as a function of frequency varying in the range mHz to MHz. From the complex impedance (Z'-Z") plot, the value of true bulk resistance is obtained. However, for the present SPE/NCPE films, Z'-Z" plots were not well-defined/unambiguous and hence, true value of bulk resistance could not be extracted. Hence, for this reason all the σ- measurements were done at one fixed (5KHz) frequency.
- **Total ionic transference number (t_{ion}) measurement:** The total ionic transference number (t_{ion}) in the newly synthesised SPE (host)/ NCPE OCC films was evaluated using a dc polarization Transient Ionic Current (TIC) technique [24]. The film was sandwiched

between two blocking SS-metal electrodes and subjected to a fixed dc potential (1V). The initial (I_T) and final (I_{ion}) currents were recorded with the help of a digital multimeter. The total ionic transference number was calculated with the help of following equation:

$$t_{ion} = \frac{I_{ion}}{I_T}$$

where I_{ion} is the current due to mobile ions (which includes both cation & anion in the polymer electrolyte systems) and I_T is total current. We obtained t_{ion} close to unity for newly synthesized SPE/NCPE films which indicated the fact that all the films materials are predominantly ionic.

➢ **Cationic transport number (t_+) measurement:** It is well known that in polymer electrolytes both cations and anions are mobile. However, for battery applications the cation transference number (t_+) is more relevant. Hence, the cation (Ag^+- and Cu^+ ion, in the present study) transference number (t_+) was evaluated using a combined ac/dc technique, suggested by Evans et al [25]. The film sample was kept between two reversible electrodes and subjected to a fixed dc polarizing potential (ΔV) for ~4-6 hours. The initial (I_0) and final (I_s) currents were recorded. AC impedance measurements were also done to evaluate the resistances: R_0(R_s) before (after) the polarization. The cation transport number (t_+) was evaluated with the help of following equation[25]:

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

3.5 All-Solid-State battery fabrication and cell performance studies: The newly synthesized SPE/ NCPE OCC films have been used as electrolyte to fabricate all-solid-state batteries in the following cell configuration:

Anode | SPE/ NCPE OCC films | Cathode

Active anode viz. Ag^+, Cu^+ in the form of thin metal foil and different cathode viz. (C+I_2+Electrolyte) in the film form have been used. The measurement of Open Circuit Voltage (OCV) and study of cell potential discharge performance have been done under varying load conditions using a high impedance digital voltmeter. The cell potential discharge profiles have been recorded as a function of time and some important battery parameters have been evaluated from the plateau region of the discharge profiles.

4. Thesis-Presentation of Ph. D. work

The total Ph.D. work done will be presented in the form of Thesis divided into six chapters. The content of the different chapters to appear in the thesis are summarized below in brief.

Chapter 1: This chapter will give an overview on the field of "**Solid State Ionics**" which includes introduction of the subject area, designing of solid state ionic materials past and present since the inception of this exotic area of research along with broad classification of solid state Ionic materials. These solid systems are popularly referred to as '**Superionic Solids**' or '**Fast Ionic Conductors**' or '**Solid Electrolytes**'. As the present research work has been mainly focused on non-lithium chemical based polymer electrolyte phase which is one of the important class of solid state ionic materials, an elaborate discussion will be made on this electrolyte phase along with their designing and broad classification. Some important theoretical models proposed for understanding the ion transport mechanism in dry polymer electrolyte systems viz. Solid Polymer Electrolytes (SPEs) and Nano Composite Polymer Electrolytes (NCPEs) will be reviewed. As mentioned in Section 2 , polymer electrolytes are potential and promising candidates to develop All-Solid-State electrochemical devices viz. batteries, fuel cell, supercapacitors, ECDs, sensors etc. Hence, at the end of the chapter, application aspects of these materials will be presented along with scope and relevance of present Ph. D. work.

Chapter 2: In this chapter, various experimental techniques used in the present investigation will be discussed along with the methods of casting of Ag^+- and Cu^+-ion conducting polymer electrolyte membranes using different procedures viz. solution cast, hot-press and high energy ball-milling. Materials /structural/ morphological characterizations have been done using XRD/SEM; spectroscopic responses have been recorded by FTIR, thermal properties have been studied by DSC while the characterization of ion transport properties of the newly synthesized SPE/ NCPE films has been done in the terms of ionic conductivity (σ) measured using ac method, total ionic transference number (t_{ion}) by a dc polarization Transient Ionic Current (TIC) technique, cationic transport number (t_+) by combined ac/dc method. At the end of the chapter, fabrication of All-Solid-State batteries based on the newly synthesized SPE (I^{st}-phase host) and NCPE OCC films will be described and the method used to characterize the electrochemical behavior of the batteries will be discussed in terms of Open Circuit

Voltage (OCV) measurement and cell-potential discharge performance studies under varying load conditions.

Chapters 3 & 4: These chapters will discuss the results of experimental investigations on non-lithium chemical based SPE/NCPE membranes viz. SPE films: (PEO: $AgCF_3SO_3$), and (PEO: $AgClO_4$); NCPE films: (PEO: $AgCF_3SO_3$) + x Al_2O_3, and (PEO:$AgClO_4$) + x TiO_2, prepared by hot-press casting technique. The optimum conducting SPE films have been identified by salt concentration dependent conductivity studies. Using these SPE film compositions as I^{st}-phase host and nano filler materials: Al_2O_3 and TiO_2 as II^{nd}-phase dispersoid, NCPE films have been hot-press synthesized. From the filler particle concentration dependent conductivity measurements NCPE OCC films have been identified. Some of the optimized SPE/NCPE films have also been prepared by traditional solution cast method for comparing the quality and σ_{rt} – values with those of hot-press cast films. SPE (I^{st}-phase host) and NCPE OCC films have been subjected to various characterization studies using the experimental techniques, mentioned in Chapter 2 and the results have been interpreted appropriately. Finally, at the end of the chapters the results of cell-potential discharge performances have been presented and discussed.

Chapter 5: In this chapter, the results of an additional study on nano-ionic effect, which may give rise to a further enhancement in the room temperature conductivity in dry polymer electrolyte, are presented. Additional SPE films based on PEO as polymeric host and $C_2H_3CuO_2$ as complexing salt have been hot-press synthesised. The optimum room temperature conducting SPE film has been identified as before. The dry powder mixture of this film composition has been subjected to high energy ball-milling for different duration viz. 0, 2,4,6,8,10,12,14 hrs, prior to hot-press casting. It was observed that σ_{rt} of milled SPE films increased initially with milling time, attained a peak value and then decreased. The peak value of σ_{rt} of milled SPE film has been significantly larger than that of unmilled SPE film. This σ_{rt} enhancement has been attributed as a definite consequence of nano-ionic effect introduced through high energy ball-milling. Finally, this SPE film has been subjected to various characterization studies as before and the results have been discussed/interpreted appropriately.

Chapter 6: This chapter will summarize the total work done in this Ph.D. programme, presented in the preceding five chapters, once again.

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(A) List of Publication in Referred Journals:

1. "Ag^{+} –ion Conducting Nano–Composite Polymer Electrolytes (NCPEs): Synthesis, Characterization and All–Solid–Battery Studies", **Rehana Ashrafi**, Dinesh K. Sahu**,** R. C. Agrawal, *J. of Non-Crystalline Solids* **391** (2014) 91–95.(Content of this paper appeared in Chapter 3).
2. "Ion Transport Characterization and Cell Potential Discharge Performance Studies on Hot-press Casted Solid Polymer Electrolyte (SPE): [(1-x) PEO: x Ag (ClO_4)]" R. C. Agrawal, **Rehana Ashrafi**, Dinesh K. Sahu, Y. K. Mahipal, Alok Bhatt, *Indian J. Pure & Appl. Physics* **51** (2013) (Content of this paper appeared in Chapter 4).
3. "Investigation on Ion transport Property of Hot-press Cast Mg^{2+} -Ion Conducting Nano-Composite Polymer Electrolyte (NCPE) Membranes: Study of Effect of Active/ Passive Filler Particle Dispersal on Conductivity" R. C. Agrawal*, Dinesh K. Sahu, Y. K. Mahipal, **Rehana Ashrafi**, *Indian J. Pure & Applied Physics* **51** (2013)
4. "Investigations on Ion Transport Properties of Hot-Press Cast Magnesium Ion-Conducting Nano-Composite Polymer Electrolyte (NCPE) films: Effect of Filler Particle Dispersal on Room Temperature Conductivity" R. C. Agrawal, Dinesh K. Sahu, Y. K. Mahipal, **Rehana Ashrafi,** *J. of Materials Chemistry & Physics* **139** (2013) 410-415.
5. "Materials and ion transport property characterization study on hot-press synthesized Solid Polymer Electrolyte (SPE) film: (PEO: KIO_3)", R. C. Agrawal, Y. K. Mahipal, **Rehana Ashrafi**, *Solid State Ionics,* **192** (2011) 6-8

(B) Paper Published in Conference Proceedings:

1. "Electrical and electrochemical properties on Mg^{2+}-ion conducting polymer electrolyte membranes" R. C. Agrawal*, Dinesh K. Sahu, Y. K. Mahipal, **Rehana Ashrafi**. 'Proc. 13th Asian Conf. on Solid State Ionics, 17-20 July, 2012Japan' (World Scientific, 2012),

2. "Conductivity enhancement in Ti_{O2} dispersed Nano-composite Polymer electrolyte (NCPE) Films: [(80PEO: 20Mg ($CF_3SO_3)_2$] + Ti_{O2} and Study of All- Solid- State Cell Performance" R. C. Agrawa**l***, Dinesh K. Sah**u,** Y. K. Mahipal, **Rehana Ashrafi,** 'Proc. 4th Int. Conf. on Electroactive Polymer: Materials and Devices' Suresh Chandra (Series Ed.), (MacMillan Pub. India 2012) p 297.

3. "Electrical property studies on hot-press synthesized nano-composite polymer electrolyte (NCPE) membranes: [70PEO: 30 $MgSO_4$] +SiO_2" R.C.Agrawal*, **Rehana Ashrafi,** Y.K.Mahipal, 'Proc.12th Asian Conf. on Solid State Ionics: Fundamental Research and Technological Applications' (Eds) B.V.R. Chowdhari, wuhan, P.R.China (2010) p. 874.
4. "Ion transport property studies on hot-press synthesized ion conducting solid polymer electrolytes: (1-x) PEO: x NaP_{O3}" R. C. Agrawal, Y. K. Mahipal, Dinesh Sahu, **Rehana Ashrafi,** 'Proc. 5^{3rd} National Symposium on Solid State Physics 53 (2008) (DAE-BRNS, India) p. 951.

(C) Participation in National/International Conference/Workshop:

1. 13th 'Asian Conference on Solid State Ionics' (ACSSI-2012), 17-20 July, 2012, Sendai, Japan (Paper presented "Electrical and electrochemical properties on Mg^{2+}-ion conducting polymer electrolyte membranes" R. C. Agrawal, Dinesh K. Sahu, Y. K. Mahipal, **Rehana Ashrafi**).
2. "Ag^{+} - Ion Conducting Nano-Composite Polymer Electrolytes (NCPEs): Synthesis, Characterization and All-Solid-Battery Studies". Rehana Ashrafi, Dinesh K. Sahu, R. C. Agrawal* Accepted for presentation in forth coming, International Conference on Solid State Ionics (ICSSI) Tokyo Japan, during 2-7, June, 2013.
3. "Investigation on Fumed Silica Dispersed Mg^{2+}-ion Conducting Nano Composite Polymer Electrolytes (NCPEs): [80PEO: 20$Mg(CF_3SO_3)_2$] + xSiO_2" R. C. Agrawal*, Dinesh K. Sahu, Rehana Ashrafi, Abstract Submitted International Conference on Materials for Advanced Technologies (ICMAT), 30 June to 5 July, 2013 in Singapore.
4. Cell-Potential Discharge Performances on All-Solid-State Batteries Based on Polymer Electrolytes", R. C. Agrawal*, D. K. Sahu, **Rehana Ashrafi**, International Conference on Recent Trends in High-Tech Materials and Nanotechnology, Department of Applied Physics, RCET, Bhilai, Chhattisgarh, (India) during February 8-9, 2013.
5. International Workshop on Advance Material and Astrophysics, Pt. Ravishnakar Sukla University Raipur (C.G.) during Feb. 19-21, 2012.
6. 9th 'National Conference on Solid State Ionics' (NCSSI-9), 15-17 Dec., 2011, Jaypee Institute of Information Technology, Noida, New Delhi, India (Paper presented

"Investigations on ion Transport Property of Hot-press Casted Mg^{2+} -ion Conducting Nano-Composite Polymer Electrolyte (NCPE) Membranes: Study of Effect of Active/ Passive Filler Particle Dispersal on Conductivity" R. C. Agrawal, Dinesh Sahu, Y. K. Mahipal, **Rehana Ashrafi)**

7. "Ion Transport Characterization and Cell Potential Discharge Performance Studies on Hot-press Casted Solid Polymer Electrolyte (SPE): [(1-x) PEO: x Ag (ClO_4)]" R. C. Agrawal, **Rehana Ashrafi**, Dinesh K. Sahu, Y. K. Mahipal, Alok Bhat. 9th 'National Conference on Solid State Ionics' (NCSSI-9), 15-17 Dec., 2011, Jaypee Institute of Information Technology, Noida, New Delhi, India.

8. 'Workshop on Electronic and Ionic Materials and Devices', 25-27 March, 2011, BHU, Varanasi (U. P.) India. (Participated)

9. 4th 'International Conference on Electroactive Polymers: Devices & Materials, Nov. 21-26, 2010, Surajkund, New Delhi, India (Paper presented "Conductivity enhancement in TiO_2 dispersed Nano-composite Polymer electrolyte (NCPE) Films: [(80PEO: 20Mg (CF_3SO_3)$_2$] + TiO_2 and Study of All- Solid- State Cell Performance" R. C. Agrawal*, Dinesh K. Sahu, Y. K. Mahipal, **Rehana Ashrafi).**

10. Workshop on 'Physical Techniques for the Investigation of Fast Ion Conducting Materials' 20-22 March, 2010, M. S. Univ., Baroda, Vadodara (Gujtat) India. (Participated)

11. " Ion Transport Property and All-Solid-State Battery Studies on Hot-Press Casted Nano-Composite Polymer Electrolyte Membrane: [92PEO: 8NaI] + 5 SiO2" R.C.Agrawal*, Y.K.Mahipal, **Rehana Ashrafi,** Dinesh sahu. was presented in 4th Internationals Conference on Electroactive Polymers: Materials and Dives during Nov. 21-26, 2010, at Surajkund (India).

12. 8th 'National Conference on Solid State Ionics' (NCSSI-8), Dec. 7-9, 2009, Dr. H. S. Gaur University, Sagar (M. P) India (Paper presented "Investigations on Ion Transport Behavior in Hot-pressed Nano Composite Polymer Electrolyte (NCPE) Membranes: [80 PEO: 20 Mg (CF_3SO_3)$_2$] + x SiO_2" R. C. Agrawal, Dinesh Sahu, Y. K. Mahipal, **Rehana Ashrafi**).

13. 'National conference on Condensed Matter Days', 26-28 Aug. 2008, Jadavpur University Kolkata, (W. B.) India (Paper presented "Ion transport property studies on hot–press synthesized Solid Polymer Electrolytes (SPEs) membranes: (1-x) PEO: x Mg $(CF_3SO_3)_2$" R. C. Agrawal, Dinesh Sahu, Y. K. Mahipal, **Rehana Ashrafi**, Alok Bhat).

14. "Investigation on Ion Transport Property Studies on Hot-press Synthesized Solid Polymer Electrolyte Membranes: (1-x) PEO: x Mg $(CF3SO_3)_2$" R.C.Agrawal*, **Rehana Ashrafi.** Dinesh sahu, Y.K.Mahipal. (was presented), CMDAYS, 26-28th Aug, 2009, Jadavpur University Kolkata.

15. "Characterization of Materials and Structural Properties on Hot-Press Synthesized Solid Polymer Electrolytes (SPE): (75PEO: 25$NaNO_3$) and Nano-Composite Polymer Electrolyte (NCPE): (75PEO:25$NaNO_3$) + SiO_2 Membranes" R.C. Agrawal*, Y.K.Mahipal, **Rehana Ashrafi,**.(was presented) 8th National Conference on Solid State Ionics (8th NCSSI), Dr. H. S. Gaur University, Sagar during Dec. 7-9, 2009.

16. "Investigation on Ion Transport Behavior in Hot-Pressed Nano Composite Polymer Electrolyte (NCPE) Membranes: [80PEO: 20Mg $(CF3SO_3)_2$] + x SiO_2" R.C.Agrawal*, D.K. Sahu, Y.K.Mahipal. **Rehana Ashrafi.** 8th National Conference on Solid State Ionics (8th NCSSI), Dr. H. S. Gaur University, Sagar during Dec. 7-9, 2009.

17. "Materials and Ion Transport Property Studies on Hot-Press Casted Solid Polymer Electrolyte membranes: [(1-x) PEO: x KIO_3]", R.C.Agrawal*, Y.K.Mahipal **Rehana Ashrafi.**, was presented in 17th International Conference on Solid State Ionics was hold in Toronto, Canada during 28th June-03rd July, 2009.